Photodetachment of H^- near a metal surface

Dehua Wang (王德华)*, Yongjiang Yu (于永江), and Hongrun Wang (王洪润)

School of Physics and Electronic Engineering, Ludong University, Yantai 264025

**E-mail: jnwdh@sohu.com*

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By using the closed orbit theory, the photodetachment cross section of H^- near a metal surface is derived and calculated. The results show that the metal surface has great influence on the photodetachment process. As the ion-surface distance is very large, the influence of the electrostatic image potential caused by the metal surface becomes small and can be neglected. The period, action, and length of the detached electron's closed orbit are nearly the same as the case of the photodetachment of H^- near an elastic interface. However, with the decrease of the ion-surface distance, the influence of the metal surface becomes significant. The amplitude of the oscillation in the photodetachment cross section becomes complicated. Each resonance peak in the Fourier transformed cross section is associated with one electron's closed orbit. Unlike the case of the photodetachment of H^- near an elastic interface, the length of the closed orbit does not equal the twice distance between the ion and the surface. But with the increase of the ion-surface distance, the length of the closed orbit approaches the case of the closed orbit near an elastic interface, which suggests the correctness of our method. This study provides a new understanding on the photodetachment process of H^- in the presence of a metal surface.

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Interactions of Rydberg atoms, ions, and molecules with metallic surfaces have attracted much attention in recent years[1−3]. It is found that as the atoms, ions, and molecules approach the surface, the Rydberg electron is subjected to fields caused by the presence of image charges in the metal, therefore this physical phenomenon is closely related to the external field behavior of atoms, ions, and molecules. In these systems, the metal surface appears as an external perturber of the electronic motion, with the atom-surface distance d as the parameter. Over the last decade, many researchers have studied the problem of Rydberg atom near a metal surface. Among them, the closed orbit theory has been provided to be a clear framework to understand the oscillation in the complicated spectra for atoms near a metal surface[4]. Contrary to many studies of the Rydberg atom near a metal surface, the photodetachment of negative ion near a metal surface has attracted little attention. Early experiment and theory showed that the photodetachment cross section of H^- in the presence of external field displays oscillatory structures and a number of authors have analyzed this phenomenon theoretically at the quantum and the semiclassical levels[5−9]. Very recently, Yang *et al.* applied closed orbit theory to study the photodetachment of negative ion near an elastic interface[10]. Later, many authors have studied the photodetachment of H^- near an elastic interface in different external fields[11−13]. In these early studies, the interface is always considered as an elastic wall, the interaction potential between the electron and the surface is neglected and the collision of the electron with the surface is elastic. Therefore, this system is a real integrable one and the classical motion of the detached electron is analytically, its theoretical treatment is relatively easy. In fact, the elastic wall is only a simple model, which is different from a metal surface[4]. For the photodetachment of negative ion near a metal interface, the method used in these early studies does not suit. Since the electron is subjected to the fields caused by the presence of image charges in the metal after being detached, this system becomes a nonintegrable one. Its theoretical analysis is complicated. In this letter, by using the closed orbit theory, we study the photodetachment of H^- near a metal surface. We obtain an analytical expression for the cross section, which is a smooth background term plus a cosine oscillating term. Formally, this formula is like the one given by Yang *et al.*[10], but the parameters in the formulas are different. In order to show the relation between the photodetachment cross section and the detached electron's classical closed orbit, we make a Fourier transformation of the cross section for this system. Each peak in the Fourier transformed cross section corresponds to the length of one detached electron's closed orbit going out from and returning to the nucleus.

The schematic plot of the system can be described as follows. The H^- ion sits at the origin with the active electron loosely bound by a short-range, spherically symmetric potential $V_{\rm b}(r)$, where r is the distance between the active electron and the nucleus. A z-polarized laser is used for the photodetachment. A metal surface perpendicular to the z axis is placed at $z = d$. So the photodetached electron can be reflected by the metal surface. According to the electrostatic image method[14], the potential acting on the detached electron in the ion-metal system can be described as $V = V_c + V_i$, in which V_c is the interaction potential of the electron with the image nucleus, which is also a short-range potential, V_i is the interaction potential between the detached electron and the image electron, $V_i = -\frac{1}{4(d-z)}$. Therefore, the Hamiltonian of H^- ion near a metal surface has the following form (in cylindrical coordinates and atomic units):

$$H = \frac{1}{2}(P_\rho^2 + \frac{l_z^2}{\rho^2}) + \frac{1}{2}P_z^2 + V_{\rm b}(r) + V_c - \frac{1}{4(d-z)}, \quad (1)$$

where P_ρ and P_z are the components of the electron's

momentum along the ρ and z directions, l_z is the z component of angular momentum.

The effect of the short-range potential of the nucleus and the image nucleus can be ignored after the electron is detached[7]. Owing to the cylindrical symmetry, the z component of angular momentum is conserved. Since $l_z = -\mathrm{i}\hbar\frac{\partial}{\partial\varphi}$, if we write the wave function in the cylindrical coordinates (ρ, z, φ), then the φ motion is separated from that in the (ρ, z) plane. Therefore, the system is reduced to a problem with two degrees of freedom. Here we consider the case of $l_z = 0$. By solving the Hamiltonian motion equations, we find the motion in the ρ direction is free: $\rho(t) = R\sin\theta + k\sin\theta t$, here R is the initial spherical radius, θ is the outgoing angle of the detached electron, and $k = \sqrt{2E}$ is the momentum. According to the closed orbit theory, every classical orbit of the detached electron that subsequently returns to the ion produces an oscillation in the photodetachment cross section. Since the ρ motion is free, only the trajectory emanating up in the z direction can be reflected back by the metal surface to the origin.

The photodetachment process of H^- near a metal surface can be described as follows. When H^- absorbs photon energies E_{ph}, outgoing electron waves are generated. These outgoing waves propagate to large distances. Due to the effect of the metal interface, these waves cannot propagate to infinity, some of the waves are turned back by the surface and return to the origin. Finally, the returning waves overlap with the outgoing source waves to give the interference pattern in the photodetachment cross section. According to the closed orbit theory, the photodetachment cross section can be split into two parts:

$$\sigma(E) = \sigma_0(E) + \sigma^{\mathrm{osc}}(E), \tag{2}$$

$\sigma_0(E)$ is the smooth background term without the external fields[5], $\sigma^{\mathrm{osc}}(E)$ is the oscillating term, which corresponds to the contribution of the returning wave traveling along the closed orbit:

$$\sigma^{\mathrm{osc}}(E) = -\frac{4\pi}{c}(E + E_{\mathrm{b}})\mathrm{Im}\langle D\psi_{\mathrm{i}}|\psi_{\mathrm{ret}}\rangle, \tag{3}$$

where $\psi_{\mathrm{i}}(\vec{q}) = B\mathrm{e}^{-k_{\mathrm{b}}r}/r$ is the initial wave function of the detached electron, $B = 0.31552$ is a normalization constant, and $k_{\mathrm{b}} = 0.2355883$, which is related to the binding energy E_{b} of H^- by $k_{\mathrm{b}} = \sqrt{2E_{\mathrm{b}}}$. D is the dipole operator[7]. For the z polarized light, $D = z$. ψ_{ret} is the returning part of the detached electron wave function, which represents the electron wave that propagates outwards into the external region first, then is reflected by the metal interface, and finally returns to the vicinity of the ion core along the closed orbit. In order to obtain the returning wave function associated with each closed orbit, we draw a sphere of radius $R \approx 10a_0$ (a_0 is the Bohr's radius). The outgoing wave on the surface of this sphere is then[10]

$$\psi^0(q) = -\frac{4Bk^2}{(k_{\mathrm{b}}^2 + k^2)^2}\cos\theta\frac{\mathrm{e}^{\mathrm{i}(kr-\pi)}}{kr}, \tag{4}$$

where k is the momentum of the electron.

When this wave propagates out from the surface and travels along the closed orbit, it changes in phase and amplitude. In the semiclassical approximation, the wave outside this sphere is a sum of the above outgoing wave:

$$\psi(q) = \sum_i \psi^0(q)A_i\mathrm{e}^{\mathrm{i}[S_i - \mu_i\pi/2]}, \tag{5}$$

where $S_i = \int p\mathrm{d}q$ is the action along the ith trajectory, μ_i is the Maslov index characterizing the geometrical properties of the ith trajectory, and A_i is the amplitude given as $A_i(\rho, z, \phi) = |J_i(\rho, z, 0)/J_i(\rho, z, t)|^{1/2}$, $J_i(\rho, z, t)$ is the Jacobian. Due to the classical motion of the detached electron, the amplitude is given by

$$A_i(\rho, z, \phi) = \left|\frac{P_{z0}}{P_{zt_i}}\right|^{1/2}\frac{R}{R + kt_i}, \tag{6}$$

in which t_i is the time for the electron going out from the source region and back to the origin. P_{z0} is the z component of the initial momentum, and P_{zt_i} is the momentum at time t_i . If there is no metal surface, the detached electron will propagate away from the source region near the nucleus as a spherical wave and never returns. Nevertheless, when there is a metal surface, the influence of the metal surface dominates in the external region, and some of the associated waves will be turned back by the surface. Due to the free motion in ρ direction, the only closed orbit is along the z axis. This orbit, initially traveling in the z direction, is turned back by the metal surface, and then returns to the vicinity of the nucleus to form a closed orbit. As the returning wave comes back close to the nucleus, it can be approximated by a plane wave traveling in the z direction as

$$(\psi)^i_{\mathrm{ret}}(q \approx 0) = N_i\mathrm{e}^{-\mathrm{i}kz}, \tag{7}$$

in which N_i is a constant. According to the general method given by Du *et al.*[15], we have

$$N_i = A_i\mathrm{e}^{\mathrm{i}(S_i - \pi/2)}\psi^0(q)(R, \theta = 0). \tag{8}$$

Substituting Eq. (4) into the above formula, N_i can be described as

$$N_i = i\tilde{A}_i(\rho, z, \phi)\frac{4Bk}{(k^2 + k_{\mathrm{b}}^2)^2}\mathrm{e}^{\mathrm{i}(S_i - \pi/2)}, \tag{9}$$

in which $\tilde{A}_i = \left|\frac{P_{z0}}{P_{zt_i}}\right|^{1/2}\frac{1}{kt_i}$.

The total returning wave is the sum of each returning wave. The overlap integral of the returning waves with the source wave function $\langle D\psi_i|$ gives the oscillation in the photodetachment cross section. By substituting the above formulas into Eq. (3), we get

$$\sigma^{\mathrm{osc}}(E) = \frac{2\pi^2}{c}\tilde{A}\frac{8B^2E}{(E_{\mathrm{b}} + E)^3}\cos(S). \tag{10}$$

Therefore the total photodetachment cross section can be described as

$$\sigma(E) = \sigma_0(E) + \frac{2\pi^2}{c}\tilde{A}\frac{8B^2E}{(E_{\mathrm{b}} + E)^3}\cos(S). \tag{11}$$

This is a smooth background term plus a cosine oscillating term. This formula is formally like the photodetachment cross section of H^- near an elastic interface[10],

but the parameters such as the period and the action of the closed orbit in the formula are different. In Table 1, we give the periods, actions, and lengths of the detached electron's closed orbit for the photodetachment of H^- near a metal surface and an elastic surface at different ion-surface distances.

In order to show the correspondence between the cross section and the detached electron's closed orbits, we perform the Fourier transform (FT) of the photodetachment cross section. We define the Fourier transform by

$$F(L) = \left| \int_0^{k_{\max}} [\sigma(E) - \sigma_0(E)] \times \mathrm{e}^{-\mathrm{i}kL} \mathrm{d}k \right|^2, \qquad (12)$$

where L is the geometric length of the orbit.

Using Eq. (11), we calculate the photodetachment cross section of H^- near a metal surface for different values of the distance between the ion and the surface, see Fig. 1. The results show that with the decrease of the ion-surface distance, the amplitude of the oscillation in the cross section becomes larger. In order to compare our results with the case of the photodetachment of H^- near an elastic surface, we calculate the cross section of H^- near an elastic surface by using the formula given by Yang *et al.*[10]. The results are also shown in Fig. 1. Figure 1(a) is the cross section as the ion-surface distance $d = 100$ a.u. The two results deviate greatly from each other. However, with the increase of the ion-surface distance, the difference between the two results is reduced. As $d = 2000$ a.u., the two results correspond with each other (Fig. 1(c)). When the ion-surface distance $d = 5000$ a.u., the two results are nearly the same, as we can see from Fig. 1(d). The reasons can be interpreted as follows. When the ion-surface distance is large, the image potential acting on the detached electron is very small and can be neglected. The period, action, and length of the detached electron's closed orbit are nearly the same as the case of the photodetachment of H^- near an elastic interface. For example, at $d = 5000$ a.u., the action of the closed orbit near a metal surface is $S = 1691.32$ a.u.; while near an elastic surface, the action is $S = 1717.51$ a.u. Their difference is very little. Therefore, we can use the elastic wall model to simulate the metal surface at large ion-surface distance. As we decrease the ion-surface distance, the electrostatic image potential acting on the electron increases. Therefore, the influence of the metal surface becomes significant and cannot be ignored. The period, action, and length of the detached electron's closed orbit deviate greatly from the photodetachment of H^- near an elastic interface, as can be seen from Table 1.

Table 1. Period T, Action S, and Length L of the Closed Orbit for the Photodetachment of H^- Near a Metal and an Elastic Surface with the Detached Electron's Energy E=0.4 eV for Different Ion-Surface Distance d (a.u.)

	d	100	200	300	1000	5000
Metal Surface	T	1099.99	2298.80	3285.68	11300.24	58212.86
	S	21.86	52.40	85.08	322.15	1691.32
	L	171.10	369.40	570.54	1971.09	9977.06
Elastic Surface	T	1164.47	2328.95	3493.42	11644.74	58223.71
	S	34.35	68.70	103.05	343.50	1717.51
	L	200	400	600	2000	100000

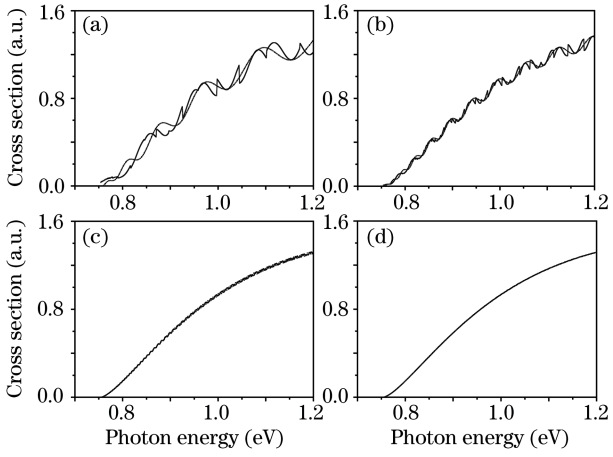

Fig. 1. Photodetachment cross section of H^- near a metal surface. The distance between the H^- and the metal surface is (a) 100 a.u.; (b) 200 a.u.; (c) 1000 a.u.; (d) 5000 a.u. The solid line is the cross section of H^- near a metal surface while the dotted line denotes the cross section near an elastic surface.

In order to show the relation between the oscillation in the photodetachment cross section and the detached electron's closed orbits, we calculated the Fourier transformed cross section of H^- near a metal surface, as shown in Fig. 2. The calculations were carried out using $k_{\max} = 0.5$ a.u. and a step size $\Delta k = 0.001$ a.u. In this system, there is only one closed orbit of the detached electron, hence there is only one peak in the Fourier transformed spectrum corresponding to the length of the closed orbit. The length of each closed orbit is also demoted in the figure, which almost equals the actual length of the closed orbit, as shown in Table 1. For example, in Fig. 2(a), the ion-surface distance is $d = 100$ a.u., the length of the closed orbit is 168.76 a.u., and the actual length of the closed orbit is 171.10 a.u.; in Fig. 2(b), $d = 200$ a.u., the length

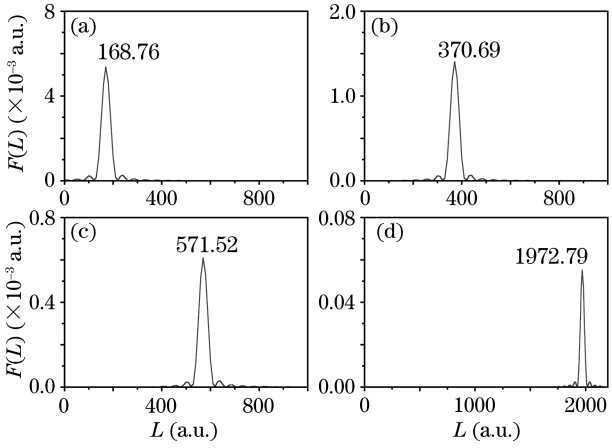

Fig. 2. Fourier transform of the photodetachment cross section of H^- near a metal surface. The distance between the H^- and the metal surface is (a) 100 a.u.; (b) 200 a.u.; (c) 300 a.u.; (d) 1000 a.u. The number beside each peak denotes the length of the closed orbit.

of the closed orbit is 370.69 a.u. and the actual length is 369.40 a.u. From this figure, we also find that unlike the case of the photodetachment of H^- near an elastic interface[12], the length of the closed orbit is not equal to the twice distance between the ion and the surface. However, with the increase of the ion-surface distance, the length of the closed orbit approaches the case of the closed orbit near an elastic interface. For instance, in Fig. 2(d), the ion-surface distance $d = 1000$ a.u., the length of the closed orbit in the Fourier transformed cross section is 1972.79 a.u., and the actual length of the closed orbit near an elastic interface is 2000 a.u. Their difference is very little. This result further suggests the correctness of our method.

In summary, we have studied the photodetachment of H^- near a metal surface by using the closed orbit theory. An analytical formula of the cross section is derived. We find that the metal surface has significant influence on the photodetachment process. Each peak in the Fourier transformed cross section corresponds to the contribution of one closed orbit. At large ion-surface distance, the metal surface can be considered as an elastic wall, its influence on the cross section can be neglected. The correspondence between our results with the one given by Yang *et al.* at large ion-surface distance suggests the correctness of our method. At present, no experiments on this system are available for comparison. We hope that our results will be useful in guiding the future experimental research of the photodetachment processes of ions in the vicinity of interfaces, cavities, and ion traps[16−18].

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